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(57) Abstract

A thickened stable hard surface cleaner comprising by weight (a) from about 10 to about 30 % abrasive particles, (b) from about 0.5 to about 2.5 % of a chlorine-containing bleach, (c) from about 0.5 to about 3 % of a thickening system comprising a cross-linked polyacrylate resin having a molecular weight in the range of 1,000,000 to 10,000,000 and a synthetic smectite clay resembling natural clays of the hectorite class, the amount of said clay being from about 20 to about 80 %, preferably from 50 to 80 %, of the thickening system, (d) from about 0.25 to about 2.0 % of a bleach stable surfactant system comprising mainly anionic surfactants, (e) from 0 to about 3 % of an electrolyte selected from the group comprising sodium or potassium carbonates or silicates, and (f) sufficient amount of sodium or potassium hydroxide to attain a pH in the range of 11.5 to 13.5.

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THICKENED SCOURING CLEANSER CONTAINING INORGANIC ABRASIVES AND HYPOCHLORITE BLEACH

This invention relates to abrasive-containing hard surface scouring cleansers containing hypochlorite bleach which are thickened with a combination of a synthetic smectite clay and a polyacrylate resin. More particularly, it relates to such compositions containing particulate abrasives which maintain high active chlorine stability over a long period of time and have good rinsability.

Polymeric thickeners are often added to liquid products containing hypochlorite bleach in order to enhance their rheological properties so as to make them more suitable for use on non-horizontal surfaces. Among the problems encountered with such compositions is the fact that liquids containing hypochlorite bleach are destructive to most synthetic and natural thickeners. In recent years, there have been developed a number of thickened bleach products incorporating, as thickeners, certain polyacrylates and certain natural or synthetic clays of the smectite type which are somewhat less subject to degradation by the hypochlorite bleach. However, many of these polymeric substances, particularly the lower molecular weight polyacrylates, do not substantially increase viscosity. Furthermore, even though these compositions may show initial stability, they tend to degrade, with a resultant loss of chlorine activity within a few months. Therefore, in commercial practice, unless these products are used within a relatively short period of time, they lose their effectiveness as cleaning agents.

The B.F. Goodrich Company produces and distributes a series of Carbopol polyacrylate resins and it is known that certain of these resins are useful in the formulation of thickened sodium hypochlorite cleaning compositions. These Carbopol resins generally promote the degradation of the available chlorine in the solutions but, but certain specific Carbopol resins are relatively stable in chlorine bleach solutions in that the rate of chlorine loss is sufficiently slow for use in thickened bleach-containing cleaning compositions.

U.S. Patent No. 4,867,896 (Elliot et al.) discloses cleaning compositions containing hypochlorite bleach thickened with cross-linked polyacrylate resins, which are said to provide improved characteristics over similar compositions thickened with certain commercially available Carbopol resins. The compositions can also include smectite or attapulgite clays. and are liquid or gel type dishwashing products and do not contain abrasive particles.

U.S. Patent No. 4,911,857 (Machin et al.) teaches the use of polyacrylates or polymethacrylates in aqueous liquid cleaning compositions comprising suspended particulate abrasive materials. The compositions can additionally contain a chlorine-releasing bleaching agent and certain Carbopol resins having molecular weights in the range of 500 to 3,000. These low molecular weight resins serve only as wetting agents. Viscosity is provided by a combination of surfactants.

European Patent Application No. 0606707 (The Clorox Company) discloses thickened hypochlorite solutions in which the principal thickening agent is a high molecular weight cross-linked polyacrylate resin. The compositions are intended for use in spray operations and do not contain abrasive particles. The principal advantage to the new compositions is their reduced bleach odor.

European Patent Application No. 0636690 (The Clorox Company) discloses similar non-abrasive compositions with sufficient amounts of surfactant added so that the compositions are gels.

European Patent Application No. 0649898 (The Clorox Company) discloses thickened bleach cleansers having abrasive particles where the thickening agent consists of a polyacrylate resin.

Many of the available thickened cleansers known in the art have sufficient thickness for use on vertical surfaces but do not have good rinsability. Thus, when such a product is used on horizontal and other non-vertical surfaces, it is often

necessary to do numerous sponge/rinse cycles in order to remove the cleanser. This problem is compounded when the cleanser contains insoluble abrasive particles. It is, of course, not practical to have separate products for vertical and horizontal surfaces. Therefore, there is a need for thickened abrasive bleach-containing cleaning compositions which will have improved rinsability.

PCT publication WO95/08619 (U.S. Patent No. 5,470,499) discloses thickened aqueous abrasive cleansers having particulate abrasives and polyacrylate resin as a thickening agent and asserts that such cleansers have good rinsability. Nevertheless, there still remains a need for thickened abrasive bleach-containing cleansers with enhanced rinsability characteristics, particularly on horizontal surfaces, and improved stability.

Natural clays of the smectite or attapulgite type have been used as thickeners in cleaning compositions. See, for example, U.S. Patents Nos. 4,396,525 (Rubin), 4,877,544 (Gabriel), 4,772,414 (Marzec), 5,348,682 (Finley) and 4,235,732 (Beyer). None of these disclosed compositions possess the desired characteristics.

Accordingly, it is a principal object of this invention to provide a thickened abrasive-containing bleach cleansing composition with enhanced stability. Further objects include providing thickened bleach compositions which do not exhibit phase separation or loss of chlorine activity over substantial periods of time.

According to the invention, there is provided a hard surface scouring cleaner composition comprising, on a weight basis.

(a) from about 10 to about 30% hard inorganic abrasive particles,

(b) from about 0.5 to about 2.5% of a chlorine-containing bleach,

(c) from about 0.5 to about 3% of a thickening system comprising a cross-linked polyacrylate resin having a molecular weight in the range of

1,000,000 to 10,000,000 and a synthetic smectite clay resembling natural clays of the hectorite class, the amount of said clay in the thickening system being from about 20% to about 80%,

(d) from about 0.25 to about 2.0% of a bleach-stable surfactant system comprising mainly anionic surfactants,

(e) from 0 to about 3% of an electrolyte selected from the group comprising sodium or potassium carbonates or silicates, and

(f) sufficient amount of sodium or potassium hydroxide to attain a pH in the range of 11.5 to 13.5.

These compositions have an apparent viscosity as measured on a Brookfield RVTDV-II with a #6 spindle at 50 rpm of 2-8 Kcps and at 1 rpm of 50-200 Kcps.

The abrasive component of the formulation is necessary for physically scouring the stains from surfaces. The abrasive agent should be present in amounts of from about 10 to about 30% by weight of the compositions; preferably, the abrasive agent is present in amounts ranging from 15 to 25%. Any suitable hard inorganic particulate base-stable abrasive agent may be used. Preferred abrasives include calcium carbonate and alumina trihydrate but harder abrasives such as a perlite, silica sand and various other insoluble, inorganic particulate abrasives can be used, such as quartz, pumice, feldspar, tripoli and calcium phosphate. Particle size will range from average particle size of about 10 to about 500 microns, preferably from 10 to 100 microns, and more preferably from 15 to 75 microns. Particle hardness of the abrasives can range from Mohs hardness of about 2-8, more preferably 3-6. Especially preferred is calcium carbonate, also known as calcite. Calcite is available from numerous commercial sources such as Georgia Marble Company, and has a Mohs hardness of about 3. Typically, a size of U.S. 140 mesh is selected, although others may be appropriate.

The scouring composition of this invention contains a chlorine oxidizing bleach derived from a hypochlorite. Generally, the hypochlorite component may be provided by a variety of sources which include sodium, potassium, lithium and calcium hypochlorites, chlorinated trisodium phosphate dodecylhydrate, potassium and sodium dichloroisocyanurate and trichlorocyanuric acid. The preferred sources are sodium or potassium hypochlorite, particularly sodium hypochlorite. The hypochlorite is present in the composition in an amount equal to about 0.5 to about 2.5% by weight of the composition. Preferably, the hypochlorite may form 0.75 to 2.0% of the composition.

Interaction of the cross-linked polyacrylate resin with the hypochlorite component of the composition is particularly important for maintaining the desirable characteristics of thickening and stability.

The hypochlorite component which is preferably present in the composition contains low levels of salts such as chlorides, which would tend to interfere with the phase stability of the composition. For this reason, the present invention avoids or minimizes the use of hypochlorite bleaches formed by methods which commonly generate large amounts of salts such as sodium chloride. Ordinary sodium hypochlorite bleach sold for laundry purposes can contain, for every 100 parts of NaOCl, up to 75 parts of NaCl. For purposes of this invention, it is preferred that the amount of NaCl present be not more than 20% of the amount of NaOCl.

In order to avoid the presence of excessive amounts of salts such as sodium chloride within the compositions, the preferred hypochlorite component is preferably selected or formed in a manner avoiding or minimizing the presence of undesirable salts. For example, ordinary sodium hypochlorite bleaches are commonly formed by bubbling chlorine gas through liquid sodium hydroxide to result in formation of the corresponding hypochlorite. However, hypochlorite bleaches produced by such reactions are undesirable for the present unless the reaction is followed by salt separation step.

In addition to the use of hypochlorites formed from the reaction of chlorine with sodium hydroxide, the present invention contemplates the use of hypochlorites formed in other ways, such as by reaction of hypochlorous acid with sodium hydroxide or other metal hydroxides in order to produce the corresponding hypochlorite with water as the only substantial by-product. Sodium hypochlorite bleach produced in this manner is available from a number of sources, for example Olin Corporation which produces sodium hypochlorite bleach as a 36% solution in water, and sold under the trademark Hy-Pure.

It is specifically contemplated that the hypochlorite component of the invention will not include chloride salt in excess of 20% of the hypochlorite. Preferably, the amount of chloride will be less than 5% by weight of the hypochlorite component.

The ionic strength of the composition has an effect on thickening. If the total ionic strength (sum of the total alkali ions plus the negative counterions) exceeds about 5 g-ions per kilogram, it becomes difficult to achieve the desired level of thickening. Moreover, ionic strength also has some effect on stability of the composition; however, the effect of ionic strength on stability is minimal relative to the effects of the cross-linked polyacrylate polymer, the synthetic clay and the polymer stabilizer. Nevertheless, the ionic strength of the compositions of the present invention should be maintained at less than about 5 g-ions/Kg, preferably less than about 3 g-ions/Kg.

In addition to enhancing the phase stability of the composition, provided primarily by the cross-linked polyacrylate polymers, the hypochlorite component also acts as a cleaning agent.

The thickening system for the compositions of this invention must include a cross-linked polyacrylate polymer of the type sold by the B. F. Goodrich Company under the trademark Carbopol and by 3V Chemical Company under the trademark Polygel. These polymeric resins should have a molecular weight in the range of

from about 1,000,000 to about 10,000,000, preferably from 1,500,000 to 5,000,000. (These molecular weight figures are based on data supplied in the manufacturers' product literature.) A particularly suitable polymeric resin is Carbopol 695, which has a published molecular weight of about 3,000,000.

These cross-linked polyacrylate polymers are generally characterized as acrylic acid polymers which are non-linear and water-dispersible while being cross-linked with an additional monomer or monomers in order to exhibit a molecular weight in the desired range. Preferably, the polymers are cross-linked with a polyalkenyl polyether, the cross-linking agents tending to interconnect linear strands of the polymer to form the cross-linked resin. It has been found that, for the purposes of achieving good long term stability, without the loss of chlorine effectiveness, the polymeric cross-linking agent must be carefully chosen within the foregoing parameters.

The thickening system comprises from about 0.5% to about 3% of the composition, preferably from 1% to 2.5% thereof.

The thickening system also comprises, in addition to the cross-linked polyacrylate polymer, from about 20% to about 80%, preferably from 50% to 80%, of its weight of a synthetic smectite-type clay similar to hectorite in structure and composition. A synthetic, rather than a natural, clay is preferably used in order to avoid degradation of the composition owing to small amounts of impurities which may be found in natural products. The preferred synthetic smectite clays for use in this invention are sold under the trademark Laponite by Southern Clay Products, Inc. Particularly useful are Laponite RD and Laponite RDS with Laponite RD being especially preferred because it contains no phosphates. In terms of the scouring compositions of this invention, the preferred amount of synthetic smectite clay is from about 0.25 to about 2.0 weight %, more preferably about 1.0% to about 2.0%. The addition of the synthetic smectite clay provides both improved rinsability, and improved stability, particularly over long time periods.

Surfactants are added to the composition for supplemental thickening and/or for non-thickening purposes such as cleaning, improved stability, etc. Stability in the presence of the hypochlorite component is the basic criterion for selecting the surfactants to be included in the composition. Generally, a wide variety of surfactants may be sufficiently stable in the presence of hypochlorite bleaches and these include betaines, sarcosinates, taurates, alkyl sulphates, alkyl sulphonates, alkyl acyl sulphonates, alkylphenol ether sulphates, alkyl diphenyl oxide sulphonates, alkyl phosphate esters, etc. Generally, the surfactant systems will comprise principally anionic surfactants, but they may also include up to about 20% of non-ionics and/or amphoterics.

Bleach-stable anionic surfactants useful in the present invention and which are especially stable in the presence of hypochlorite include water soluble alkali metal alkyl sulphates, alkyl sulphonates, alkylbenzene sulphonates, alkyldiphenyl oxide sulphonates particularly the sodium salts of those having from 8 to 18 carbon atoms in the alkyl group, and sodium alkyl sarcosinate salts in which the alkyl group is a saturated hydrocarbon chain having from 7 to 17 carbon atoms. A preferred alkyl sulphate is lauryl sulphate. A preferred sarcosinate is sodium lauroyl sarcosinate, sold by W.R. Grace & Co. under the trademark Hamposyl L30. Preferred alkyl sulphonates are the secondary alkyl products sold as Hostapur SAS by Hoechst in formulations containing 30% and 60% active ingredient. Preferred alkyldiphenyl oxide sulphonates are the products sold by Dow Chemical Company under the name Dowfax 2A1 and by Olin Corporation under the name Polytergent 2A1; both products are aqueous based and contain about 45% active ingredient which is principally sodium dodecyl diphenyl oxide disulphonate.

Examples of other organic anionic non-soap surfactants include: sodium C_{10}-C_{18} alkylsulphates such as sodium dodecylsulphate and sodium tallow alcoholsulphate; sodium C_{10}-C_{18} alkanesulphonates such as sodium hexadecyl -1,1-sulphonate, and sodium C_{12}-C_{18} alkylbenzenesulphonates such as sodium

dodecylbenzenesulphonate. The corresponding potassium salts may also be employed. The amount of surfactant in the compositions of this invention ranges from about 0.25% to about 3%, preferably from 0.5 to 2.0%.

It is also necessary to employ a stabilizer for the purpose of achieving optimum stability of the solution and for pH adjustment. A sufficient amount of sodium or potassium hydroxide should be added to provide a pH in the range of from 11.5 to 13.5, preferably from 12 to 13.

Optional ingredients in the composition include an electrolyte such as sodium or potassium carbonate or silicate, in amounts ranging up to about 3% of the composition. The principal purpose of these carbonates and silicates is to act as a buffer in order to maintain the proper pH. In addition, it has been found that, in the compositions of this invention, the presence of a small amount of sodium or potassium silicate results in somewhat improved stability. It has also been found that compositions which contain both potassium and sodium ions, derived from the various ingredients, have a somewhat higher viscosity than analogous compositions with sodium as the sole alkali metal action.

The hypochlorite composition preferably includes a bleach stable fragrance component and more preferably a bleach stable fragrance component which is relatively more volatile than the oxidants included in the hypochlorite component of the composition which are responsible for bleach odors.

The scouring compositions of the present invention together with the preferred cross-linked polyacrylate polymers for achieving combined thickening and stability may also include other components, either for enhancing one or more of these effect or for other purposes. For example, additional adjuncts in the composition may include buffers, builders, colorants, fluorescent whitening agents, pigments, etc. However, it is again noted that such adjuncts must be selected to the extent that they not substantially interfere with the preferred characteristics of the present invention as described above.

The scouring composition of the instant invention can be prepared by admixing the above-described essential and optional components together in the appropriate concentrations by any conventional means normally used to form thickened compositions. Some shear agitation is, of course, necessary to ensure preparation of the compositions of this type. It is preferred that, in the mixing process, the synthetic clay compound be kept in an alkaline slurry until the polyacrylate resin is added.

This invention will be better understood by reference to the following examples which are here included for illustrative purposes and are not intended to be limitations.

EXAMPLE 1

A scouring cleanser containing the following ingredients was prepared.

Ingredient	%
Carbopol 695	0.5%
Laponite RD	1.0
KOH	0.92
Potassium silicate solution	1.0
NaOCl	1.3
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate	1.2
Water	q.s. to 100

A 2% Carbopol gel was prepared by adding 9.0g Carbopol 695 to 441g of stirred deionized water over a ten-minute period. Agitation was provided with an overhead stirrer to provide a deep vortex and minimize clumping of Carbopol particles. Total mixing time was extended to about one hour.

Over a five-minute period, 18g of Laponite RD was added to 582g of deionized water being vigorously stirred to minimize formation of large particle aggregates. The initially opaque suspension became slightly hazy within a few minutes and stirring was continued for about thirty minutes. Samples of the concentrate were weighed out into separate reaction containers as required for the further additions.

To 66.6g of 3% Laponite gel which was being stirred in a 400 ml polyethylene beaker was added 2.0g of Kasil 6 potassium silicate solution. After 30 minutes mixing of the silicate-containing gel, 7.35g of 25% KOH was added. Stirring was

continued throughout addition of all other ingredients, which were added 5 to 10 minutes after each other. Next 16.5g of 15.9% NaOCl solution (Olin Hy-Pure N) as added, followed by 50g of 2% Carbopol 695 gel. 40g calcium carbonate (Whittaker-Clark-Daniels 823 Marblewhite 200) was then added and mixed until a smooth creamy texture was obtained. Mixing intensity was reduced so that 5.3g Polytergent 2A1 (45% actives) could be added with minimal aeration. Finally, 13g of water was added to bring the total weight to about 200g.

The pH, viscosity and bleach stability values, measured according to the methods discussed below, were as follows:

pH	12.9
Viscosity	3.6
NaOCl Stability	
days to 40% loss at 49°	37
% remaining after 10 months	80

EXAMPLE 2

Employing the process of Example 1, a scouring cleanser containing Laponite RDS clay is prepared. The ingredients of the composition are:

Ingredient	%
Carbopol 695	0.50
Laponite RDS	1.00
KOH	0.90
NaOCl	1.10
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate[1]	0.55
TiO_2	0.40
Fragrance	0.15
Water	q.s. to 100

[1] Dowfax 2A1.

In Examples 3-12, additional compositions according to this invention were prepared according to the method of Example 1 and their viscosities and bleach stabilities were measured. The sodium silicate and potassium silicate were obtained from PQ Corporation as PQ "N" Silicate and Kasil 6, respectively. The sodium hypochlorite used was Hy-Pure N, obtained from Olin Corporation, which contains 16% NaOCl, and 0.5% each of NaCl and NaOH. The dodecyl diphenyloxide disulphonate used most was derived from Polytergent 2A1. The percentages for Hostapur SAS are expressed as active ingredients.

The pH level was measured after one day at ambient temperatures (22°C). The viscosity was also measured after one day at ambient temperatures on a Brookfield #6 spindle, at 50 RPM after 30 seconds, and is given in units of Kcps.

The stability of NaOCl was measured in terms of (1) the number of days required for the composition to show 40% loss of chlorine activity on storage at 49°C, and (2) percent of available chlorine after storage for ten months at ambient temperatures (about 22°C).

EXAMPLE 3

Ingredients	%
Carbopol 695	0.5%
Laponite RD	1.0
KOH	0.84
NaOCl	1.3
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate	1.2
Water	q.s. to 100
pH	12.9
Viscosity	3.2
NaOCl Stability	
days to 40% loss at 49°	18
% remaining after 10 months	46

EXAMPLE 4

Ingredients	%
Carbopol 695	0.5%
Laponite RD	1.0
KOH	0.88
Potassium silicate solution	0.4
NaOCl	1.3
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate	1.2
Water	q.s. to 100
pH	13.0
Viscosity	3.1
NaOCl Stability	
days to 40% loss at 49°	35
% remaining after 10 months	80

EXAMPLE 5

Ingredients	%
Carbopol 695	0.5%
Laponite RD	1.0
NaOH	0.66
Sodium silicate solution	1.0
NaOCl	1.3
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate	1.2
Water	q.s. to 100
pH	13.0
Viscosity	2.4
NaOCl Stability	
days to 40% loss at 49°	34
% remaining after 10 months	86

EXAMPLE 6

Ingredients	%
Carbopol 695	0.75%
Laponite RD	0.75
KOH	1.0
NaOCl	1.3
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate	1.2
Water	q.s. to 100
pH	12.7
Viscosity	6.5
NaOCl Stability	
days to 40% loss at 49°	15
% remaining after 10 months	47

EXAMPLE 7

Ingredients	%
Carbopol 695	1.0%
Laponite RD	0.25
KOH	1.16
NaOCl	1.3
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate	1.2
Water	q.s. to 100
pH	12.7
Viscosity	5.6
NaOCl Stability	
days to 40% loss at 49°	14
% remaining after 10 months	44

EXAMPLE 8

Ingredients	%
Carbopol 695	1.0
Laponite RD	0.25
KOH	1.18
Potassium silicate solution	0.1
NaOCl	1.3
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate	1.2
Water	q.s. to 100
pH	12.7
Viscosity	5.2
NaOCl Stability	
days to 40% loss at 49°	33
% remaining after 10 months	74

EXAMPLE 9

Ingredients	%
Carbopol 695	0.5%
Laponite RD	2.0
Na_2CO_3	0.325
NaOH	0.74
NaOCl	1.2
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate	1.0
Hostapur SAS	1.0
Fragrance	0.05
Water	q.s. to 100
pH	13.1
Viscosity	2.7
NaOCl Stability	
days to 40% loss at 49°	19

EXAMPLE 10

Ingredients	%
Carbopol 695	0.5%
Laponite RD	2.0
K_2CO_3	0.425
KOH	1.04
NaOCl	1.2
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate	1.0
Hostapur SAS	1.0
Fragrance	0.05
Water	q.s. to 100
pH	13.2
Viscosity	4.5
NaOCl Stability	
days to 40% loss at 49°	20

EXAMPLE 11

Ingredients	%
Carbopol 695	0.5%
Laponite RD	2.0
NaOH	0.74
Sodium silicate solution	0.2
NaOCl	1.2
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate	1.0
Hostapur SAS	1.0
Fragrance	0.05
Water	q.s. to 100
pH	13.2
Viscosity	2.6
NaOCl Stability	
days to 40% loss at 49°	29

EXAMPLE 12

Ingredients	%
Carbopol 695	0.5%
Laponite RD	2.0
KOH	1.15
Potassium silicate solution	0.2
NaOCl	1.2
$CaCO_3$	20.0
Dodecyl diphenyloxide disulphonate	1.0
Hostapur SAS	1.0
Fragrance	0.05
Water	q.s. to 100
pH	13.1
Viscosity	6.0
NaOCl Stability	
days to 40% loss at 49°	29

CLAIMS

1. A hard surface scouring cleaner composition having an apparent viscosity as measured on a Brookfield RVTDV-II with a #6 spindle at 50 rpm of 2-8 Kcps and at 1 rpm of 50-200 Kcps, said composition comprising, on a weight basis: (a) from 10 to 30% of abrasive particles; (b) from 0.5 to 2.5% of a chlorine containing bleach; (c) from 0.5 to 3% of a thickening system comprising a cross-linked polyacrylate resin having a molecular weight in the range of 1,000,000 to 10,000,000 and a synthetic smectite clay, the amount of said clay in the thickening system being from 20 to 80%; (d) from 0.25 to 2% of a bleach-stable surfactant system comprising mainly anionic surfactants; (e) from 0 to 3% of a buffer/electrolyte selected from the group consisting of sodium or potassium carbonates or silicates, and mixtures thereof; and (f) sufficient amount of sodium or potassium hydroxide to provide a pH of from 11.5 to 13.5.

2. A composition according to claim 1 in which the amount of clay in thickening system (c) is from 50 to 80%.

3. A composition according to claim 2 in having an ionic strength of less than 5 g-ions/Kg.

4. A composition according to claim 3 in which the chlorine-containing bleach is a hypochlorite.

5. A composition according to claim 4 in which the hypochlorite is sodium hypochlorite.

6. A composition according to claim 3 comprising from 15 to 25% of inorganic abrasive particles.

7. A composition according to claim 6 in which the average size of the abrasive particles is from 15 to 75 microns.

8. A composition according to claim 3 in which the cross-linked polyacrylate resin has a molecular weight of from 1,500,000 to 5,000,000.

9. A composition according to claim 8 in which the resin has a molecular weight of about 3,000,000.

10. A composition according to claim 7 which comprises from about 0.25 to 2.0% of synthetic smectite clay.

11. A composition according to claim 10 which comprises from 1.0 to 2.0% of synthetic smectite clay.

12. A composition according to claim 8 which comprises 0.75 to 2.0% of a hypochlorite bleach.

13. A composition according to claim 12 in which the ionic strength is less than 3 g-ions/Kg.

14. A composition according to claim 12 in which the surfactant system consists of anionic surfactants and is present in an amount of from 0.5 to 1.5% of the composition.

15. A composition according to claim 14 in which the anionic surfactants are selected from the group consisting of sodium C_8 to C_{18} alkyl sulphates, sodium C_8 to C_{18} alkyldiphenyl oxide sulphonates, sodium C_8 to C_{18} alkyl sulphonates, sodium C_8 to C_{18} alkylbenzenesulphonates, sodium alkyl sarcosinate salts in which the alkyl is a saturated hydrocarbon chain having from 7 to 17 carbon atoms, and mixtures thereof.

16. A composition according to claim 4 in which the pH is from 12 to 13.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/06379

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C11D 3/12, 3/14, 3/37, 3/395, 17/08
US CL :510/369, 418, 426, 434, 476, 507
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/369, 418, 426, 434, 476, 507

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,116,849 (LEIKHIM) 26 September 1978, col. 3, lines 15-37, the EXAMPLES and the absract.	1-16
Y	US, A, 4,248,728 (PURYEAR) 03 February 1981, col. 2, lines 27-42; TABLE 1, EXAMPLE 1 and the claims.	1-16
Y	US, A, 4,911,857 (MACHIN) 27 March 1990, the Examples and the claims.	1-16
Y	US, A, 5,160,448 (CORRING) 03 November 1992, col. 3, lines 60-65; col. 5, lines 46-63; col. 6, lines 25-33 & 59-61; col. 9, lines 21-29, the EXAMPLES and the claims.	1-16
Y,P	US, A, 5,470,499 (CHOY) 28 November 1995, the abstract and claims.	1-16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 JULY 1996	03 SEP 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer for DENNIS L. ALBRECHT Telephone No. (703) 308-2525

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